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ARTICLE

Pd/C Catalyzed Phenoxycarbonylation Using *N*-Formylsaccharin as a CO Surrogate in Propylene Carbonate as a Sustainable Solvent

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This work reports the first Pd/C catalyzed phenoxycarbonylation of aryl iodides using *N*-formylsaccharin as a CO surrogate. Advantageously, the reaction could be carried out in propylene carbonate as an environmentally benign and sustainable polar aprotic solvent under CO surrogacy. Using *N*-formylsaccharin as a CO surrogate, allows the cheaper and readily available phenols as the coupling partner. A range of phenyl esters could be synthesized under mild, co-catalyst free, ligand free and additive free conditions, including multi-substituted novel phenyl esters. The Pd/C catalyst could be recycled up to four times with only a slight loss in activity. The reaction could be scaled up to gram scale synthesis.

Introduction

The synthesis of aromatic estersis an important reaction which forms part of the bulk and fine chemical industry. Aromatic esters constitute some of the most important structural motifs encountered in agrochemicals, fungicides and pharmaceutical drugs(Figure 1). They are also vital building blocks in multi-step organic synthesis.[1]

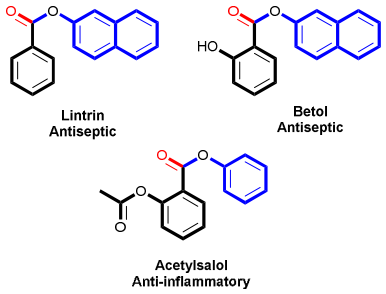

Figure 1. Representative examples of pharmaceutically important phenyl esters.

Conventionally, esters are synthesized by reacting a carboxylic acid with an alcohol/phenol in the presence of a strong mineral acid (sulfuric acid, hydrogen chloride, *p*-toluenesulfonic acid and chlorosulfuric acid) or lewis acid. Other processes include alkylation of carboxylate salts of alkali metal, alkaline-earth metal, copper and silver, acylation of alcohols with acid chlorides, acid anhydrides and ketenes, alcoholysis of nitriles and acylation of olefins with carboxylic acids.[2]However, most of these protocols suffer from use of stoichiometric or excess amount of reagents, reactive substrates and harsh conditions, thus leading to generation of large amounts of waste and poor atom economy.

In the 1970's, Heck pioneered the use of palladium catalysed carbonylative cross-coupling reaction as a powerful tool for the synthesis of carboxylic acid and its derivatives.[3] The protocol involves the conversion of an aryl/vinyl halide in the presence of carbon monoxide as a C-1 building block and a suitable *O,N*-nucleophile to afford carboxylic acid derivatives with high atom economy.Although Heck carbonylation has found diverse applications for the synthesis of a plethora of molecules, the use of gaseous CO limits the application of carbonylation at the industrial scale and in academic laboratories. This is attributed to the fact that CO is an odourless, colourless and inflammable gas whose inhalation even in ppm amount can be lethal. The need to transport and store gaseous CO in cylinders, along with specialized high pressure reactors required for handling CO and carrying out carbonylation reactions pose safety risks andfurther impede its use. These limitations can be addressed by using CO surrogates wherein carbonylation can be carried out without using gaseous CO. The chemistry of CO surrogates has gained impetus over the last decade as several surrogate molecules and improvised methodologies have been investigated for carrying out carbonylation reactions.[4]

Different CO surrogates, catalytic systems and reaction methodologies have been applied for the synthesis of aromatic esters. Skrydstrup and co-workers reported the use of 9-methyl-fluorene-9-carbonyl chloride (COgen) as a CO surrogate for the synthesis of tertiary esters[5]and activated esters[6]from aryl bromides through the two-chamber system. Oxalyl chloride[7] and very recently glyoxalic acid[8] were also usedas surrogate molecules for *ex-situ* CO generation through the two-chamber system. Molybdenum hexacarbonyl,[9] paraformaldehyde,[10] formic acid[11] and aryl formates[12]have been used for the synthesis of aromatic esters from aryl

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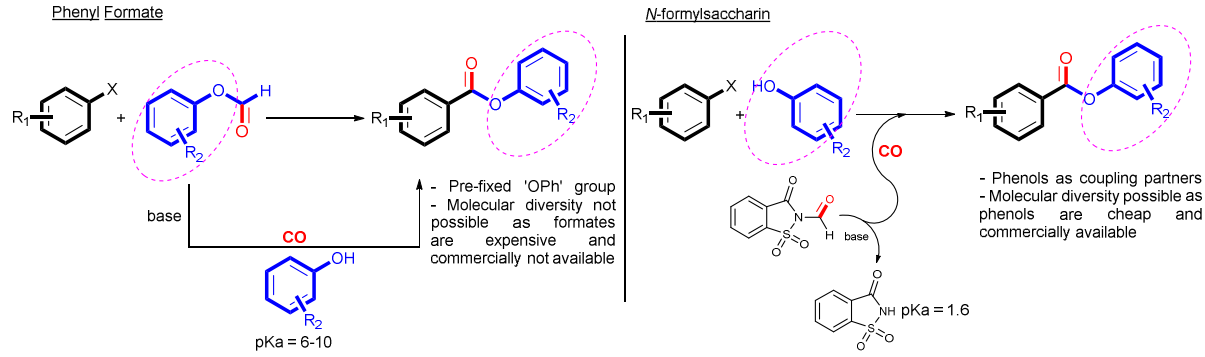
iodides, bromides and even chlorides[13] through *in situ* CO generation.

N-formylsaccharin, developed as a formylating agent,[14] was applied for the first time as a CO surrogate for the reductive carbonylation of aryl halides by Manabe and co-workers.[15] Later, the same group reported the fluorocarbonylation of aryl halides, thus leading to the synthesis of carboxylic acid derivatives in a two-step, one-pot fashion.[16] Fleischer and co-workers reported the synthesis of aliphatic esters by the alkoxycarbonylation of alkenes using *N*-formylsaccharin.[17]

Although, the synthesis of aromatic esters with aliphatic alkoxy (OR) group is well documented using different CO surrogates, the synthesis of aromatic phenyl esters has largely been carried out using phenyl formate (HCOOPh). However, while using phenyl formate as a CO surrogate, the product (phenyl ester) ends up with the pre-installed phenoxy (OPh) group present in the formate. This limits the synthesis of diverse phenyl esters and makes the process commercially not viable as the more expensive formate esters are used as the coupling partners as compared to the economical and readily available phenols.*N*-formylsaccharin after decarbonylation results in the formation of saccharin. Since saccharin has comparatively lesser nucleophilicity (pK_a = 1.6) as compared to phenol (pK_a = 6-10), we envisaged that the use of *N*-formylsaccharin as a CO surrogate would allow the application of phenols as coupling partners in phenoxycarbonylation reactions (Scheme 1).



Scheme 1. Comparison of the decarbonylation of phenyl formate and *N*-formylsaccharin.

Traditionally, phenoxycarbonylation reactions using CO surrogates have been carried out under homogeneous catalytic protocols. Although, advantageously, the cheaper aryl bromides have been used as coupling partners, most of the reaction methodologies suffer from high catalyst loading, use of phosphine ligands, stoichiometric amount of additives.Further, reactions using *N*-formylsaccharin have been carried out in polar aprotic *N*,*N*-dimethylformamide[15,16] (*N*,*N*-DMF) and dichloromethane.[17] Although, *N*-formylsaccharin is known to readily undergo decarbonylation in the aforementioned solvents, amide and chlorinated solvents are considered unsustainable and hazardous. Moreover, in contemporary chemistry, the impact and consequence of reaction solvents on human health and environment needs to be carefully considered. Under REACH[18] (Registration, Evaluation, Authorisation and Restriction of CHemicals), a regulation which addresses the production and use of chemical substances, along with their potential impact on human health and environment, the usage of solvents will be subjected to scrutiny and/or restricted in the near future. We thus endeavoured to identify an alternate sustainable polar aprotic solvent.

Organic carbonates, especially cyclic carbonates, have gained prominence as environmentally friendly solvents in synthetic chemistry.[19] They are biodegradable, non-toxic, odourless, possess low vapour pressure and synthesized at the industrial scale at very low costs.[20] Moreover, greener and sustainable methodologies have been established for their synthesis from renewable feedstocks. This thus makes them eco-friendly and further increases their potential as benign solvents in organic synthesis. The GlaxoSmithKline

Figure 2. Structures of **(1)** ethylene carbonate and **(2)** propylene carbonate.

(GSK) solvent selection guide rates ethylene and propylene carbonate (Figure 2)good to excellent, thus showing no points of concern across all criteria.[21] Furthermore, as compared to *N*,*N*-DMF, ethylene and propylene carbonate have higher boiling points (low vapour pressure), thus resulting in lower atmospheric emissions and making them safer to store and handle. Since cyclic carbonates are comprised of only carbon, hydrogen and oxygen, they do not produce oxides of nitrogen and sulfur on combustion or incineration. Ethylene carbonate being a solid at room temperature is disadvantageous to use. However, propylene carbonate being a liquid, is a benign and sustainable alternative to *N*,*N*-DMF and dichloromethane. Despite these advantages, organic carbonates have only been seldom used in carbonylation reactions.[22]

Homogeneous catalytic protocols suffer from catalyst product separation and the inability to recycle the catalyst.

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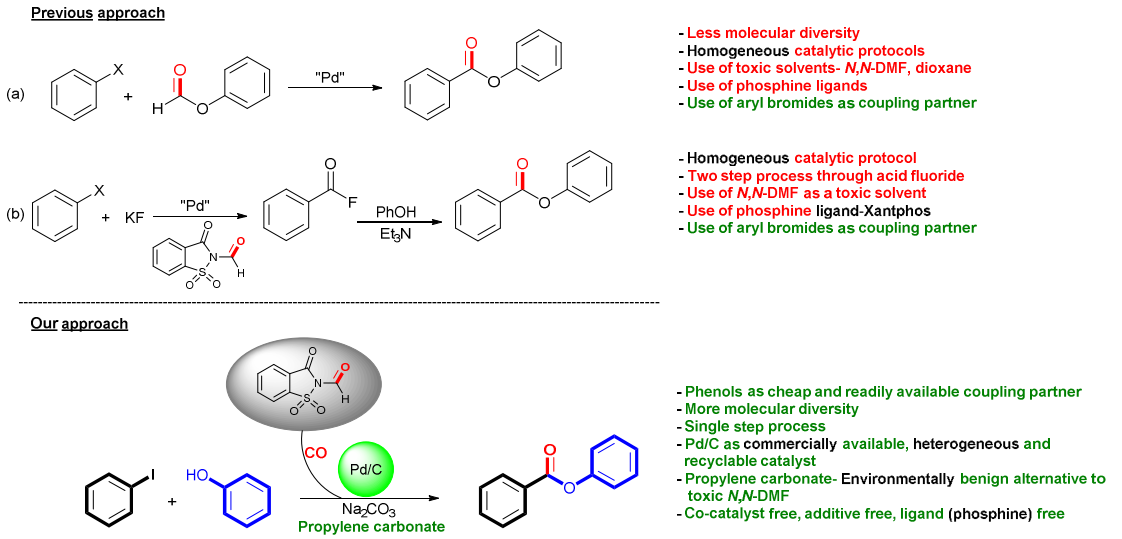
Palladium on activated charcoal (Pd/C) is a commercially available and inexpensive heterogeneous catalyst which addresses the problems associated with homogeneous catalysis. Further, Pd/C is seldom explored as a catalyst in CO surrogate chemistry.[23]Considering our continued interest in Pd/C catalyzed carbonylation reactions,[24] we herein report the first Pd/C catalysed phenoxycarbonylation of aryl iodides using *N*-formylsaccharin as a CO surrogate in propylene carbonate as an environmentally benign and sustainable solvent (Scheme 2).

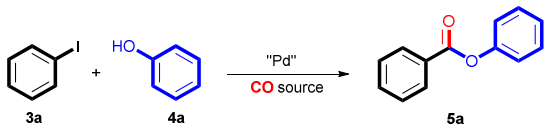


Scheme 2. Comparison of previous reaction protocols with the current protocol.

Results and Discussion

We carried out the reaction optimization by monitoring the carbonylative cross-coupling reaction between iodobenzene**3a** and phenol**4a**thus leading to the synthesis of phenyl benzoate **5a**(Table 1).Initially we carried out the reaction using $Pd(OAc)_2$ and $PdCl_2$ as homogenous palladium precursors

Table 1. Optimization of reaction parameters.[a]



Entry	[b]Pd source (mol%)	Ligand (mol%)	Base	CO source	CO source concentration (mmol)	Solvent	Time (h)	Temperature (°C)	Conversion[c] (%)	Selectivity[c] (%)
Effect of palladium source										
1	$Pd(OAc)_2$ (3 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	95	100
2	$PdCl_2$ (3 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	71	95
3	Pd/C (3 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	32	100
4	Pd/C (5 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	45	100
Effect of base										
5	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	90	100

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6	Pd/C (5 mol%)	PPh_3 (10 mol%)	Et_3N	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	16	79
7	Pd/C (5 mol%)	PPh_3 (10 mol%)	K_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	70	100
8	Pd/C (5 mol%)	PPh_3 (10 mol%)	K_3PO_4	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	59	100
9	Pd/C (5 mol%)	PPh_3 (10 mol%)	TMEDA[d]	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	21	100
Effect of time										
10	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	12	100	66	100
11	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	18	100	87	100
12	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	24	100	90	100
Effect of temperature										
13	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	18	60	56	100
14	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	18	80	85	100
15	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	18	100	87	100
Effect of ligand loading										
16	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	18	80	85	100
17	Pd/C (5 mol%)	PPh_3 (5 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	*N*,*N*-DMF	18	80	84	100
Effect of solvent										
18	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	Toluene	18	80	06	100
19	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	1,4-dioxane	18	80	10	100
20	Pd/C (5 mol%)	PPh_3 (10 mol%)	Na_2CO_3	*N*-formylsaccharin	0.50	Propylene carbonate	18	80	90	100
21	**Pd/C (5 mol%)**	**–**	**Na_2CO_3**	*N*-formylsaccharin	0.50	**Propylene carbonate**	**18**	**80**	**76**	**100**
22	Pd/C (5 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.50	Ethylene carbonate	18	80	67	100
Effect of CO source										
23	Pd/C (5 mol%)	–	Na_2CO_3	Gaseous CO	1 bar	Propylene carbonate	18	80	99	100
24[e]	Pd/C (5 mol%)	–	Na_2CO_3	Phenyl formate	0.50	Propylene carbonate	18	80	79	100
25	Pd/C (5 mol%)	–	Na_2CO_3	Formalin	0.50	Propylene carbonate	18	80	02	–
26	Pd/C (5 mol%)	–	Na_2CO_3	Paraformaldehyde	0.50	Propylene carbonate	18	80	–	–
Effect of *N*-formylsaccharin concentration										
27	Pd/C (5 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.25	Propylene carbonate	18	80	30	100
28	Pd/C (5 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.30	Propylene carbonate	18	80	45	100
29	Pd/C (5 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.50	Propylene carbonate	18	80	76	100
30	Pd/C (5 mol%)	–	Na_2CO_3	*N*-formylsaccharin	0.60	Propylene carbonate	18	80	78	100

[a] Reactions conditions: **3** (0.25 mmol), **4** (0.25 mmol), base (0.5 mmol), solvent (2 mL).[b] 10% Pd/C.[c]Conversion and selectivity were based on iodobenzene and determined by GC-MS. [d] TMEDA = *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine. [e] Phenol was not added.

in *N*,*N*-DMF and the reaction proceeded with 95% and 71% conversion respectively. Subsequently, we replaced the palladium precursor with heterogeneous 10% Pd/C (3 mol%) and observed a 32% conversion with a complete

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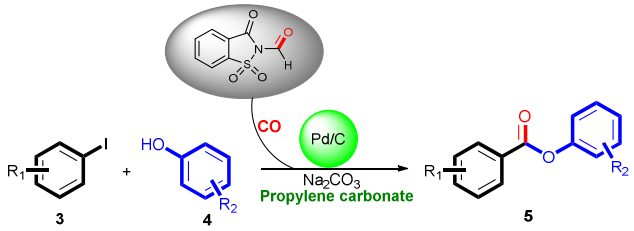
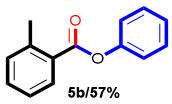
selectivity towards **5a**. Increasing the amount of catalyst to 5 mol% lead to a marginal increase in conversion from 32% to 45% (Table 1, entries 1-4).

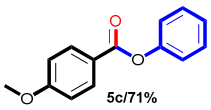
In order to increase the conversion of **3a** towards **5a**, we studied the effect of base and ligand. Addition of 10 mol% of PPh_3 increases the conversion to 90% when Na_2CO_3 is used as the base. However, changing the base to Et_3N brings down the conversion drastically to 16% with a decrease in selectivity as well. Other inorganic (K_2CO_3 and K_3PO_4) and organic bases (TMEDA) gave inferior conversion and selectivity as compared to Na_2CO_3 (Table 1, entries 5–9). Next, we studied the effect of time and temperature on the conversion. Decreasing the reaction time to 12 h brings down the conversion to 66%, but when the reaction is carried out for 18 h, 87% conversion was observed at 100 °C. The conversion falls to 56% when the reaction temperature is brought down to 60 °C. However, at 80 °C, when the reaction is carried out for 18 h, 85% conversion was observed (Table 1, entries 10-15). Decreasing the PPh_3 loading from 10 mol% to 5 mol% gave an almost similar conversion (Table 1 entries 16 and 17). The solvent study revealed that the reaction does not proceed in non-polar solvents (Table 1, entries 18 and 19). We were delighted to observe that the reaction proceeded under ligand-free conditions in propylene carbonate to give a 76% conversion. Ethylene carbonate gave a lower conversion as compared to propylene carbonate (Table 1 entries 20-22). Moreover, being a solid, ethylene carbonate is difficult to handle. Hence propylene carbonate was chosen as the solvent of choice.

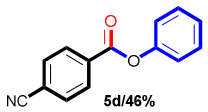
Subsequently, we studied the effect of different sources of CO, including gaseous CO. While using gaseous CO (1 bar). It gives 99% conversion and 100% selectivity towards **5a**. When phenyl formate was applied as a CO source, a comparable conversion to *N*-formylsaccharin with complete selectivity towards **5a** was obtained. However, the reaction did not proceed in the presence of formalin and paraformaldehyde as sources of CO (Table 1, entries 23-26). Since *N*-formylsaccharin would allow the use of phenols as coupling partner, it was chosen as the surrogate of choice. We also studied the effect of concentration of *N*-formylsaccharin on the conversion and selectivity. Using 0.25 mmol and 0.30 mmol of *N*-formylsaccharin brings down the conversion to 30% and 45% respectively (Table 1, entries 27 and 28). However, increasing the concentration to 0.60 mmol does not have any profound effect on the conversion (Table 1, entry 30). Hence, 0.50 mmol of *N*-formylsaccharin was chosen as the optimised concentration (Table 1, entry 29).Having established the optimised conditions, we focussed our attention on the scope of different phenyl esters that could be synthesized under the developed protocol (Table 2).

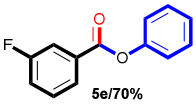
Table 2. Scope of the Pd/C catalyzed phenoxycarbonylation using *N*-formylsaccharin.[a]

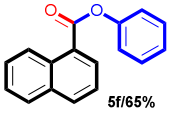


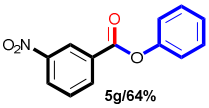
1.[c]  5b/57%

2.[c]  5c/71%

3.[c]  5d/46%

4.[b]  5e/70%

5.[b]  5f/65%

6.[b]  5g/64%

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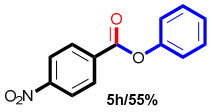
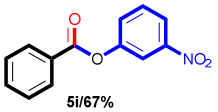
7.[b]



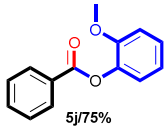
5h/55%

8.[b]



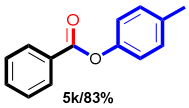
5i/67%

9.[b]



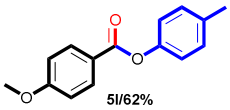
5j/75%

10.[b]



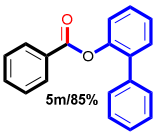
5k/83%

11.[c]



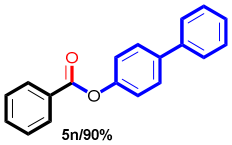
5l/62%

12.[b]



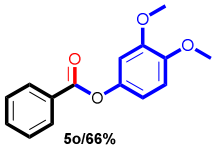
5m/85%

13.[b]



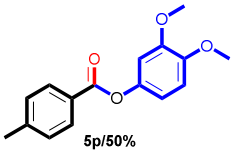
5n/90%

14.[b]



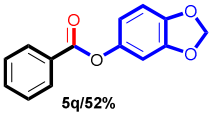
5o/66%

15.[b]



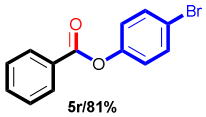
5p/50%

16.[b]



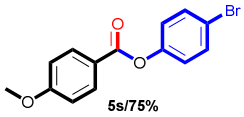
5q/52%

17.[b]



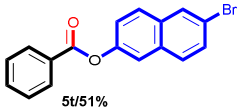
5r/81%

18.[b]



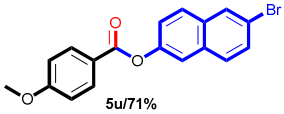
5s/75%

19.[b]



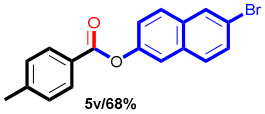
5t/51%

20.[b]



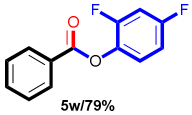
5u/71%

21.[b]



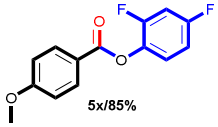
5v/68%

22.[b]



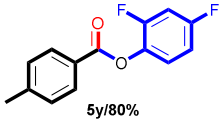
5w/79%

23.[b]



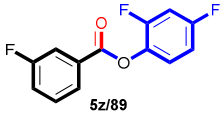
5x/85%

24.[b]



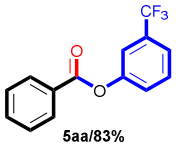
5y/80%

25.[b]



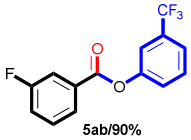
5z/89

26.[b]



5aa/83%

27.[b]



5ab/90%

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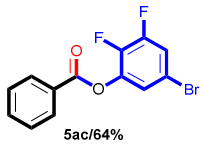
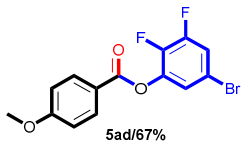
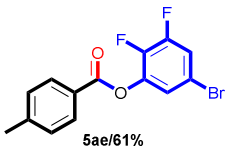
28.[b] 29.[b] 30.[b]



5ac/64%

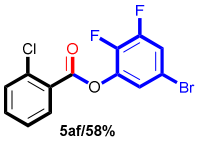


5ad/67%

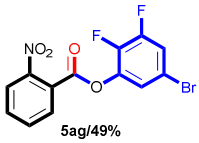


5ae/61%

31.[b] 32.[b]



5af/58%



5ag/49%

[a] Reaction conditions: **3**(0.25 mmol, **4**(0.25 mmol), Na_2CO_3 (0.5 mmol), *N*-formylsaccharin (0.5 mmol), propylene carbonate (2 mL), 10% Pd/C (5 mol%) at 80 °C for 18 h. [b] Isolated yield. [c] GC-MS yield.

Electron-donating substituents, *ortho*-methyl and *para*-methoxy, present on the aryl iodide could be coupled with phenol to give the phenyl esters **5b** and **5c** in 57% and 71% yields respectively (Table 2, entries 1 and 2). Electron-withdrawing substituents, *para*-cyano, *meta*-fluoro, *meta*- and *para*-nitro on the aryl iodidewere also smoothly coupled to yield the phenyl esters**5d**, **5e**, **5g** and **5h** in 46%, 70%, 64% and 55% yields respectively (Table 2, entries 3, 4, 6 and 7). Phenyl 1-naphthoate (**5f**) could be synthesized in 65% yield from phenol and 1-iodonaphthalene (Table 2, entry 5). 3-nitrophenol, guaiacol (2-methoxyphenol) and *para*-cresol were transformed into the phenyl esters **5i**, **5j**, **5k** and **5l** in 67%, 75%, 83% and 62% yields respectively (Table 2, entries 8-11). Biphenyl esters **5m** and **5n** were synthesized in 85% and 90% yields respectively by carbonylatively coupling 2-phenylphenol and 4-phenylphenol with iodobenzene (Table 2, entries 12 and 13).3,4-Dimethoxyphenyl esters, **5o** (66%) and **5p** (50%), could be synthesized from 3,4-dimethoxyphenol, and ester **5q**(52%), containing a 3,4-methylenedioxy unit could be synthesized from sesamol (Table 2, entries 14-16). *Para*-bromophenyl esters, **5r** and **5s**, and 6-bromonaphthyl esters, **5t**, **5u** and **5v**, could be synthesized in yields ranging from 51% to 81% (Table 2, entries 17-21).

Organo-fluorine compounds form a vital backbone of pharmaceutically active drug molecules and are considered very important in medicinal chemistry.[25] 2,4-Difluorophenyl esters, **5w**, **5x** and **5y** were synthesized by carbonylatively coupling 2,4-difluorophenol with the corresponding aryl iodide in 79% to 85% yields respectively (Table 2, entries 22-24). The trifluoro phenyl ester, 2,4-difluorophenyl-3-fluorobenzoate, **5z**, was synthesized by carbonylatively coupling 2,4-difluorophenol and 1-fluoro-3-iodobenzene in 89% yield (Table 2, entry 25). Phenyl esters, **5aa** and **5ab**, containing the trifluoromethyl substituent were synthesized in 83% and 90% yields respectively (Table 2, entries 26 and 27). The phenol bearing fluoro and bromo substituents, 5-bromo-2,3-difluorophenol, was carbonylatively coupled with the corresponding aryl iodides to afford the halo substituted esters, **5ac**, **5ad** and **5ae**, in 61% to 67% yields (Table 2, entries 28-30). Phenyl ester **5ad** was isolated as a crystalline solid and the structure was elucidated by single crystal X-ray crystallography (Figure 3).1-chloro-2-iodobenzene and 1-iodo-2-nitrobenzene could be carbonylatively coupled with 5-bromo-2,3-difluorophenol to afford the ester, **5af**, bearing chloro, bromo and fluoro substituents and ester **5ag** in 58% and 49% yields respectively (Table 2, entries 31 and 32). Notably, multi-substituted esters, **5af** and **5ag** may represent potential building blocks in organic synthesis.

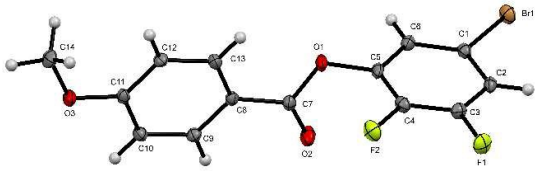


Figure 3. ORTEP diagram of phenyl ester **5ad**.

The phenoxycarbonylation of 4-bromoanisole and 4-chloroanisole under the optimized reaction conditions did not yield the corresponding phenyl esters. The aryl halides failed to undergo any conversion and were recovered as such.

Next, we focussed our attention on the recyclability of Pd/C under CO surrogacy. Given the high cost of palladium and catalyst-product separation problems associated with homogenous catalytic protocols, recycling palladium will bring down the overall cost of the process, thus making the protocol economically viable and sustainable. The reaction between iodobenzene (**3a**) and phenol (**4a**) leading to the synthesis of phenyl benzoate (**5a**) was chosen as the model reaction for checking the recyclability. After the fresh run, the reaction mixture was centrifuged at 10,000 rpm for 15 min and Pd/C was separated from the reaction mixture, washed with ethyl acetate to remove traces of the product and dried at 100°C overnight. The dried Pd/C was applied

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for the next run after charging with substrates, *N*-formylsaccharin and propylene carbonate. Notably, Pd/C could be recycled up to four times with only a marginal decrease in conversion (Figure 4).

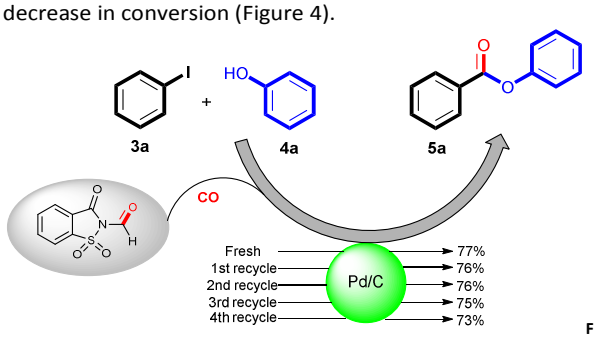
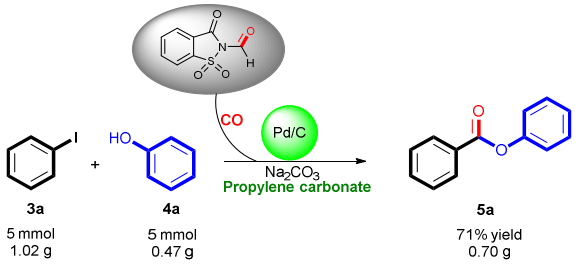


Figure 4. Recyclability study of Pd/C catalyzed phenoxycarbonylation using *N*-formylsaccharin.

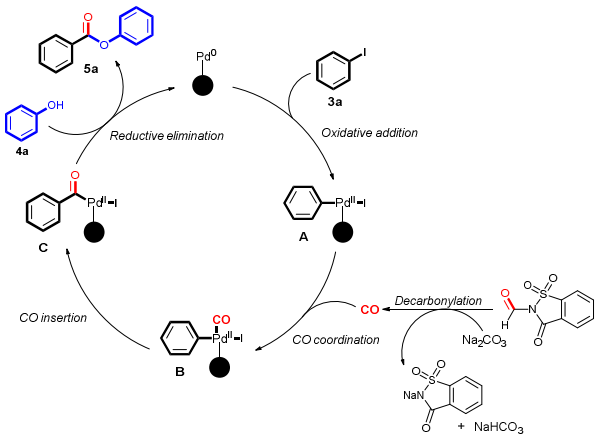
The ICP-AES analysis of the reaction mixture separated from the catalyst by centrifugation after the fourth recycle showed that the palladium content was less than 0.1 ppm, thus indicating negligible palladium leaching.

A scale up experiment (gram scale) was carried out to study the present protocol. Delightfully, the reaction between iodobenzene (**3a**) and phenol (**4a**) could be carried out at gram scale resulting in the synthesis of phenyl benzoate (**5a**) in 71% yield (Scheme 3).



Scheme 3. Gram scale Pd/C catalyzed phenoxycarbonylation using *N*-formylsaccharin.

The mechanism for the Pd/C catalyzed carbonylative synthesis of phenyl esters using *N*-formylsaccharin as the CO surrogate is shown in Scheme 4. The aryl iodide (**3a**) undergoes oxidative addition to the Pd(0) centre resulting in the aryl palladium species **A**. *N*-formylsaccharin undergoes decarbonylation in the presence of Na_2CO_3 and the CO released coordinates to the aryl palladium species to give **B**. Subsequent CO insertion gives **C** which reacts with phenol (**4a**) to afford the phenyl ester product (**5a**). Simultaneous reductive elimination regenerates Pd(0) for the next catalytic cycle.



Scheme 4. Proposed mechanism for the Pd/C catalyzed phenoxycarbonylation using *N*-formylsaccharin as the CO surrogate.

Conclusions

In conclusion, we have established the first Pd/C catalyzed phenoxycarbonylation of aryl iodides using *N*-formylsaccharin as a CO surrogate in propylene carbonate as an environmentally benign and sustainable polar aprotic solvent. The methodology does not require the need for gaseous CO and a high pressure reactor. The protocol uses Pd/C as a commercially available, recyclable, heterogeneous catalyst. Advantageously, the protocol is a one-step process and is co-catalyst free, ligand free and additive free. A range of phenyl esters could be synthesized under mild conditions, including novel multi-substituted ester molecules. The Pd/C catalyst could be recycled up to four times under CO surrogacy and the process could be scaled up to gram scale synthesis. The use of Pd/C in combination with propylene carbonate, thus represents a green and sustainable methodology for the synthesis of phenyl esters.

Experimental Section

General

All chemicals and solvents were purchased from different commercial sources and were used as received without further purification. The progress of the reaction was monitored by GC-MS and thin layer chromatography using Merck silica gel 60 F254 plates. The products were visualized with a 254 nm UV lamp. The GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (d_f) = 0.25 µm) (column flow 2 mL min^{-1}, 100 °C to 240 °C at 10 °C min^{-1} rise) was used for the mass analysis of the products. Products were purified by column chromatography on 100–200 mesh silica gel. The ^{1}H and ^{19}F NMR spectra were recorded on 500 MHz spectrometers in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. The ^{13}C NMR spectra were recorded on 125 MHz spectrometers in $CDCl_3$. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane as an internal standard and

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J(coupling constant) values were reported in hertz. The splitting patterns of protons are described as s (singlet), d (doublet), dd (doublet of doublets), t (triplet) and m (multiplet). High resolution mass analysis was performed on quadrupole-time of flight Bruker MicroTOF-Q II mass spectrometer equipped with an ESI and APCI source. Single crystal X-ray diffraction was done on a Bruker D8 VENTURE diffractometer equipped with CMOS Photon 100 detector and Mo-Kα (λ = 0.71073 Å) radiation was used.

Typical procedure for Pd/C catalyzed phenoxycarbonylation of aryl iodide using *N*-formylsaccharin as a CO surrogate

To a 15 mL pressure tube, aryl iodide (0.25 mmol), phenol (0.25 mmol), Na_2CO_3 (0.5 mmol), *N*-formylsaccharin (0.5 mmol), 10% Pd/C (5 mol%, 13 mg) were added. Subsequently, 2 mL of propylene carbonate was added to the reaction mixture. The reaction mixture was stirred at 80 °C for 18 h. After completion of the reaction, the reaction mixture was centrifuged for 15 mins at 10,000 rpm. Pd/C was separated from the reaction mixture and washed with 2 mL ethyl acetate to remove traces of the product.The combinedmixture was subjected to column chromatography (silica gel, 100–200 mesh size) with petroleum ether–ethyl acetate as the eluent to afford the pure product.

Scale up experiment

To a 100 mL pressure tube, iodobenzene (5 mmol, 1.02 g), phenol (5 mmol, 0.47 g), Na_2CO_3 (10 mmol, 1.06 g), *N*-formylsaccharin (10 mmol, 2.11g), 10% Pd/C (5 mol%, 260 mg) were added. Subsequently, 20 mL was added to the reaction mixture. The reaction mixture was stirred at 80 °C for 18 h. After completion of the reaction, the reaction mixture was centrifuged for 15 mins at 10,000 rpm. Pd/C was separated from the reaction mixture and washed with (2 × 5 mL) ethyl acetate to remove traces of the product.The combined mixture was subjected to column chromatography (silica gel, 100–200 mesh size) with petroleum ether–ethyl acetate as the eluent to afford phenyl benzoate (0.70 g, 71% yield) as the pure product.

Recycling study

To a 15 mL pressure tube, iodobenzene (0.25 mmol, 51 mg), phenol (0.25 mmol, 24 mg), Na_2CO_3 (0.5 mmol, 53 mg), *N*-formylsaccharin (0.5 mmol, 106 mg), 10% Pd/C (5 mol%, 13 mg) were added. Subsequently, 2 mL of propylene carbonate was added to the reaction mixture. The reaction mixture was stirred at 80 °C for 18 h. After completion of the reaction, the reaction mixture was centrifuged for 15 mins at 10,000 rpm. Pd/C was separated from the reaction mixture and washed with 2 mL ethyl acetate to remove traces of the product and dried at 100 °C overnight. The dried Pd/C was applied for the next run after charging with substrates, *N*-formylsaccharin and propylene carbonate. The product yields were calculated by subjecting the reaction mixture at each cycle to GC-MS analysis.

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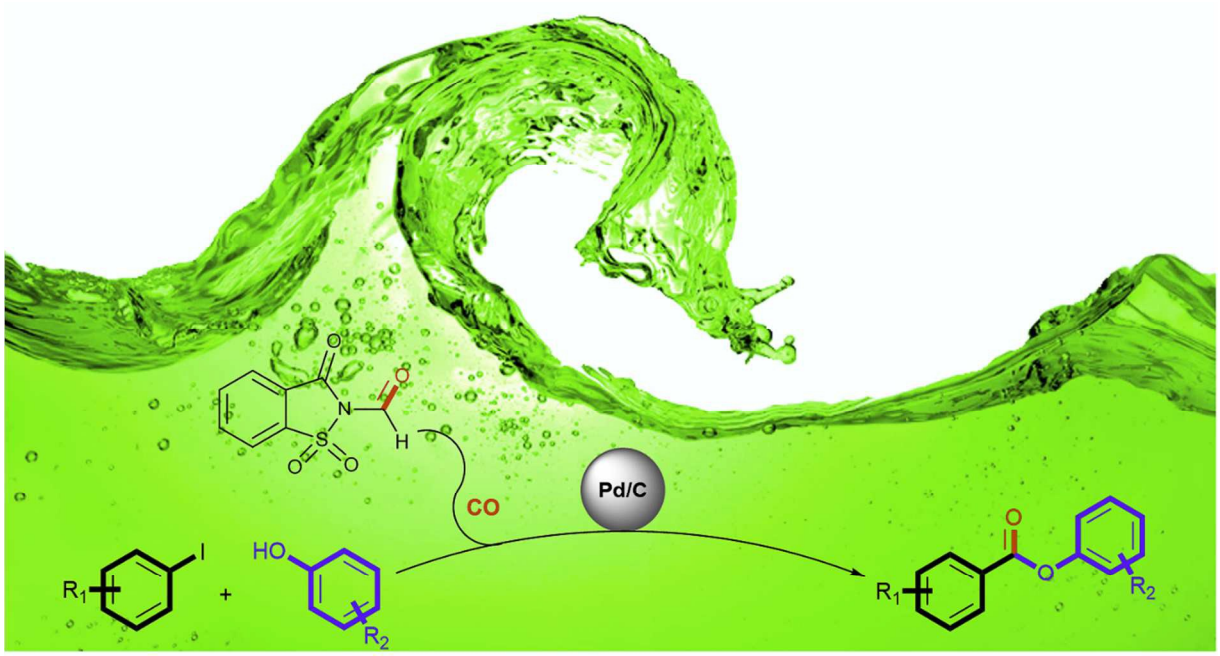
Graphical Abstract



Recyclable and commercially available Pd/C catalyzes the phenoxycarbonylation reaction using *N*-formylsaccharin as a CO surrogate in propylene carbonate as an environmentally benign and sustainable polar aprotic solvent under co-catalyst free, ligand free and additive free conditions.